

Effect of second metal (Cu, Co) on catalytic performance of bimetallic Ni-based catalyst for phenol HDO

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The conversion of biomass to renewable liquid fuels has received considerable attention for partly replacing conventional fuels and environmental concern. Converting biomass to liquid fuels (called bio-oil) via fast pyrolysis or hydrothermal treatment helps to increase volumetric and energy density and also to reduce transportation costs.¹ However, the direct use of bio-oil for combustion engine/turbine has some implications because of different properties of bio-oil compared with conventional fossil fuels. More than 200 compounds in bio-oils are known, having various types of functional groups with specific chemistry. Furthermore, water accounts for 15-30 wt%.¹ Therefore, upgrading of bio-oil is necessary to improve its properties and to make it suitable for further use. Among the available upgrading strategies, hydrodeoxygenation (HDO) is considered as interesting new technology.²

The development of suitable catalysts for this process is challenging up to now due to high coke formation and rapid deactivation at hydrothermal condition. Many researchers have applied conventional catalysts such as hydrodesulfurization (HDS) catalysts (CoMo/Al₂O₃, NiMo/Al₂O₃)³⁻⁴ and hydrotreating catalyst based on supported noble metal such as Pt, Pd or Ru).⁵⁻⁶ However, the first class of catalysts showed low activity and partly deactivation due to large water content in bio-oil. The latter class of catalysts presented high activity and stability, but their application is limited due to high costs. Apart from that, non-noble metal supported catalysts, mostly based on Ni, have been reported.⁷⁻⁹ Although these catalysts were also active, coke deposition on the catalyst was still the problem.⁸

To overcome the above drawbacks of previous catalysts, we have developed non-sulfided, non-noble bimetallic catalysts for bio-oil HDO. Two catalyst series (Ni-Cu/HZSM-5 and Ni-Co/HZSM-5) with different metal ratios and monometallic Ni, Cu and Co reference catalysts were prepared by incipient wetness impregnation. The catalysts have been denoted as xNi_yCu or xNi_zCo, where x, y, z are the rounded contents (wt%) of nickel, copper

and cobalt, respectively. The prepared catalysts were characterized by ICP, N₂-physisorption, TPR, XRD, XPS, IR and TEM. To demonstrate the deoxygenation efficiency and to understand the effect of the second metal on bimetallic catalysts, phenol was used as a model compound for bio-oil. The hydrodeoxygenation performance of the prepared catalysts was evaluated in batch runs (25 ml autoclave, 0.5 g of phenol, 10 ml of H₂O, 250 °C, 0.025g catalyst, 2 h reaction time).

The N₂-physisorption studies showed that the specific surface areas of all prepared bimetallic catalysts were more or less the same (Table 1). Moreover, IR results also showed that total acidities were very similar. The addition of both Cu and Co to Ni/HZSM-5 strongly promoted Ni reduction as observed in TPR profiles, i.e., reduction was possible at lower temperature. According to further characterization of the catalysts by TEM, XRD and XPS, the formation of Ni-Cu and Ni-Co alloy was observed in Ni-Cu/HZSM-5 and Ni-Co/HZSM-5 catalysts, respectively, with different effect compared to Ni/HZSM-5 catalyst. Substitution of Cu caused a loss of active sites at the surface (by dilution of Ni), and Cu tended to segregate at the surface with larger particle size, leading to lower Ni dispersion. On the other side, the presence of Co caused smaller particle sizes and strongly stabilized the active Ni sites on the surface and therefore Ni dispersion on the catalyst surface was increased.

Table 1 - Textual properties of catalysts

Catalysts	S _{BET} (m ² /g)*	V _t (cm ³ /g)**	Catalysts	S _{BET} (m ² /g)	V _t (cm ³ /g)
HZSM-5	405	0.37	16Ni4Cu	280	0.33
21Ni	281	0.29	11Ni10Cu	271	0.28
21Cu	278	0.27	10Ni10Co	271	0.25
19Co	281	0.24	5Ni14Co	272	0.31

*S_{BET}: surface area; **V_t: total pore volume.

The activity test results showed that Ni/HZSM-5 showed significantly higher activity compared to both Cu/HZSM-5 and Co/HZSM-5 catalysts. The substitution of any fraction of Cu to Ni/HZSM-5

significantly reduced catalytic activity, whereas the addition of Co preserved high activity (Figure 1). This result can be explained with the discussed solid state properties of these catalysts.

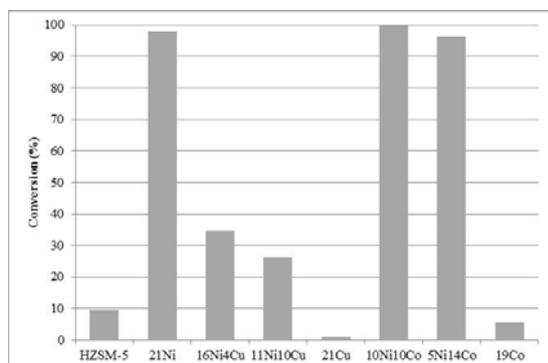


Fig. 1 - Activity of the pure support and prepared catalysts.

Regarding the selectivity, Ni-Co/HZSM-5 showed better performance than Ni/HZSM-5 in terms of the selectivity to saturated hydrocarbons (Figure 2). Among the prepared catalysts, 10Ni10Co showed the best catalytic performance with 99.3% selectivity to hydrocarbons at almost complete phenol conversion.

Furthermore, the coke deposition of spent catalysts was also checked by CHN analysis. The results shown in Figure 2 reveal that the Ni-Co/HZSM-5 strongly decreases the coke formation compared to Ni/HZSM-5.

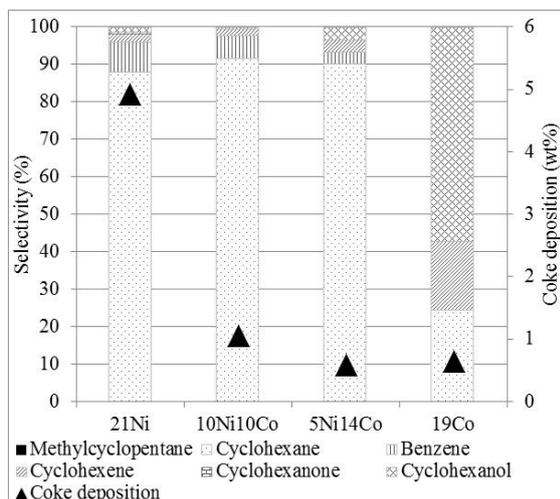


Fig. 2 - Product distribution and coke deposition (triangles point to values of the right y-axis) on Ni-Co/HZSM-5.

In summary, we have developed highly active, non-sulfided, non-noble bimetallic catalysts based on Ni-Co alloy supported on HZSM-5. In addition to enhanced catalytic performance, 10Ni10Co strongly reduces the amount of coke deposition. The catalyst

activity seems to be linked to Ni dispersion at first, whereas other parameters like oxidation state or nature of second metal may also affect selectivity. These findings might open a novel opportunity for effective upgrading of bio-oil. Such investigations are currently in progress.

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References

- 1 D. Mohan, C.U. Pittman, and P.H. Steele, *Energy & Fuel*, **2006**, 20, 848-889.
- 2 Graça, J.M. Lopes, H.S. Cerqueira, and M.F. Rebeiro, *Ind. Eng. Chem. Res.*, **2013**, 52, 275-287.
- 3 E. Laurent and B. Delmon, *J. Catal.*, 1994, 146, 281.
- 4 Y. Romero, F. Richard, and S. Brunet, *Appl. Catal. B*, **2010**, 98, 213.
- 5 J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, *Ind. Eng. Chem. Res.*, **2009**, 48, 10324.
- 6 A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause, *Catal. Today*, **2009**, 147, 239.
- 7 C. Zhao, J.A. Lercher, *Angew. Chem., Int. Ed.*, **2012**, 51, 1.
- 8 X. Zhang, T. Wang, L.L. Ma, Q. Zhang, T. Jiang, *Biore. Technol.*, **2013**, 127, 306.
- 9 P.M. Mortensen, J.D. Grunwaldt, P.A. Jensen, and A.D. Jensen, *ACS Catal.*, **2013**, 3, 1774.